



Research article

Effects of mineral matter and temperatures on conversion of carboxylic acids and their derivatives during pyrolysis of brown coals

Jia-Wei Kou^{a,b}, Zong-Qing Bai^{a,*}, Jin Bai^a, Zhen-Xing Guo^a, Wen Li^a^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China^b Key Laboratory of Coal Science and Technology Co-founded by Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, PR China

ARTICLE INFO

Article history:

Received 21 July 2015

Received in revised form 23 March 2016

Accepted 1 June 2016

Available online 10 June 2016

Keywords:

Brown coals

Oxygen-containing functional groups

Pyrolysis

Kinetics

Mineral matter

ABSTRACT

Oxygen-containing functional groups and mineral matter play important roles in thermal conversion of brown coals, but little attention has been paid to the effects of mineral matter on the conversion kinetics of oxygen-containing functional groups. In this work, silicon-containing mineral compounds (quartz and clays) and cations were removed by treatments of HF and HCl aqueous solutions, respectively. Thereafter, curve-fitting technique was used to analyze spectra measured by in-situ diffuse reflectance infrared Fourier transformation (DRIFT) technique during pyrolysis. The results show that first-order kinetic model is suitable for describing elimination of carboxylic acids and their derivatives, but formation of some compounds, such as anhydrides and phenolic esters of aliphatic acids (RCOOAr), accords with kinetic model with higher reaction order (two or three). Cations catalyze the decomposition of carboxylic dimers and thus promote the formation of anhydrides and RCOOAr, resulting in small decrease in amounts of anhydrides and RCOOAr at high temperatures. Clays and quartz (CAQ) restrain the elimination of carboxylic acids and their derivatives by impeding diffusion of volatile matters outwards into surrounding atmosphere. CAQ also suppress the formation of RCOOAr by obstructing contact among oxygen-containing functional groups.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

High concentration of oxygen (ca. 25–30 wt%, dry basis) is one of the specific characteristics of brown coal. Generally, oxygen-containing groups in brown coals are phenolic hydroxyl, carboxyl, ester, and carbonyl groups. The carboxylic acids and their derivatives have attracted much interest since they account for a large portion of the total oxygen in brown coals [1]. Moreover, the carboxylic acids and their derivatives not only relate to ion-exchanging properties of brown coals and high moisture content in them [2], but also affect the thermal conversion (pyrolysis, gasification and liquefaction) of brown coals. Accordingly, investigation of pyrolysis behavior of carboxylic acids and their derivatives will deepen the understanding of coal pyrolysis and promote the utilization of brown coals.

Generally, the carboxyl groups of brown coals start to decompose in the range of 150–250 °C. According to contents of carboxyl groups determined by ion-exchanging, Murray [3] concluded that 70% of the carboxyl groups decomposed at 300 °C and 92% at 600 °C. However, the later work of Schafer showed that the contents of carboxyl groups in char was underestimated at 300 °C, because decreasing porosity of char inhibited the access of ion-exchanging reagents [4]. In fact, the

work of Schafer indicated that only about 30% of the carboxyl groups were decomposed at 300 °C. In addition to decomposition, carboxyl groups may lead to condensation and esterification reactions during coal pyrolysis. Brooks et al. [5] found that water was produced by esterification reactions of carboxylic acids and phenols in brown coals below 300 °C. Artok et al. [6] suggested that a general reaction pathway for carboxylic acids involves formation of anhydrides in the absence of water. The esterification and condensation reactions produced additional linkage among structural units of brown coals and hence resulted in suppression of tar formation. Murray [7] observed that decomposition rates reached to maxima near 400 °C for carboxylic acids and near 600 °C for carboxylates, indicating that the cations exchanged onto the carboxyl groups improved the thermal stability of the latter.

In general, it is believed that mineral matter acts as catalysts during coal pyrolysis [8,9]. The natural clays, mainly aluminosilicate, catalyzed transferring of H₂ to coals during hydrolysis [10]. The catalysis of clays may arise from the diluting effect of quartz and inert components in clays on impeding agglomeration of coal particles [11,12]. In other words, clays inhibited the cross-linking reactions between functional groups by obstructing their contact. Therefore, it was difficult to determine any catalytic effects of clays during hydrogenation due to their physical function as a diluter [13]. Cations, mainly alkali and alkaline-earth ions associated with carboxyl groups, are another important inorganic matter in coals. They also showed some catalytic action during

* Corresponding author.

E-mail address: baizq@sxicc.ac.cn (Z.-Q. Bai).

pyrolysis of bituminous coals [14]. Unlike bituminous coals, tar yield decreased with increasing contents of cations during pyrolysis of brown coals [15], and cations had remarkable effects on the aromatic/aliphatic composition of tar [16]. The effects of cationic components are mainly reflected in the following aspects: activities in cracking oxygen-containing functional groups into CO and CO₂ molecules [17,18], promoting release of aliphatic materials [19], and hindering release of larger aromatic molecules [20]. In addition, inherent minerals have significant effect on emission of sulfur and nitrogen during coal pyrolysis [21,22].

Infrared spectroscopy is potentially a powerful tool for the characterization of coals. However, infrared analysis has been limited by the overlap and superposition of the complex functional groups in coals. Therefore, least-squares curve-fitting technique is widely used to resolve infrared spectra of coals, and the quantification and semi-quantification of functional groups in coals are largely improved due to the application of the technique. Supaluknari et al. [23] found the presence of esters, carboxylic acid and ketonic groups in coals by the use of least-squares curve-fitting technique in carbonyl stretching region of infrared spectra (1800–1500 cm⁻¹). Cronauer et al. [24] and Tahmasebi et al. [25] also applied the technique to study the changes in compounds containing carbonyl groups (e.g. carboxylic acid, esters, carboxylates and anhydrides) during drying of brown coals. Through measuring corresponding peak area of curve-fitted infrared spectra, the technique can be employed to determine apparent aromaticity of coals [26] and quantify aromatic and aliphatic CH groups [27], carbonyl groups [28,29], hydroxyl groups [30] as well as various hydrogen bonds [31] in coals. The works mentioned above demonstrate that the curve-fitting technique is effective for characterization and quantification of functional groups in coals. The utilization and reliability of the curve-fitting technique have been described in some reviews [32,33].

Despite a lot of studies carried out in the past, there is some lack of knowledge about the mechanisms and kinetics during the pyrolysis of brown coals, especially reaction kinetics of oxygen-containing functional groups in brown coals. In particular, to the best of our knowledge, there has been no systematic report on the combined effects of heating and mineral compounds (cations, clays and quartz) on the pyrolysis kinetics of carboxylic acids and their derivatives in brown coals. In this work, diffuse reflectance infrared Fourier transformation (DRIFT) spectroscopy was employed to measure the in-situ infrared spectra of brown coals with and without clays and quartz (CAQ) or cations during pyrolysis, and curve-fitting technique was applied to analyze the infrared bands of carboxylic acids and their derivatives. By analyzing the kinetic data, we studied the conversion of carboxylic acids and their derivatives during pyrolysis of brown coals and found the effects of mineral matter on their reaction kinetics.

2. Experimental

2.1. Sample preparation

Two Chinese brown coals, Xiaolongtan (XLT) and Huoliuguole (HLGL), were used with particle sizes under 74 μm, and properties of the two coals are shown in Table 1. Inductively coupled plasma atomic

emission spectrometry (ICP-AES) was used to analyze the ash composition of raw and demineralized coal (DMC). As shown in Table 2, there exist higher K, Na, Ca, and Mg contents for XLT coal and higher Si and Al contents for HLGL coal, which indicates cationic components and CAQ are rich in XLT and HLGL coals, respectively. Thus, HLGL and XLT coals were subjected to the treatment of HCl and HF aqueous solution, respectively, so that CAQ remained in HLGL coal and cations in XLT coal. These treatments highlight the effect of mineral matter in question and avoid the influence of the other mineral matter.

In order to remove cations in coals, 10 g of HLGL coal were poured into 100 mL of HCl aqueous solution (5 mol/L) and stirred for 24 h under nitrogen atmosphere with a magnetic stirrer. The residual coal was filtered and washed with distilled water effectively until no chloride ion was detected. XLT coal was subjected to the treatment of HF aqueous solution (5 mol/L) by the same procedure to remove CAQ in the coal. Subsequently, the same procedure was applied with HCl and HF aqueous solutions (5 mol/L) in succession to remove the most of the mineral compounds (i.e. cations and CAQ) in both coals. The DMC submitted to the treatments of HF and/or HCl aqueous solutions were denoted as XLT (HF), HLGL (HCl), HLGL (HCl HF), and XLT (HF HCl) samples, respectively. “HF” or “HCl” mean that CAQ or cations were selectively removed by the treatment of HF or HCl aqueous solution, respectively. Similarly, “HCl HF” or “HF HCl” means that clays, quartz and cations were removed by leaching of HCl and HF aqueous solution. The proximate and ultimate analyses of the DMC are also listed in Table 1. It is well-known that HCl aqueous solution is efficient to remove cations but invalid to remove CAQ. On the contrary, diluted HF aqueous solution is good to remove CAQ but inefficient to remove cations. As shown in Table 1, the major mineral matter in XLT coal was removed by treatment of HCl aqueous solution, indicating cations are the main mineral components in XLT coal. On the analogy of this, CAQ are the main mineral components in HLGL coal. After HCl/HF treatment, most mineral matters (e.g. carbonate, oxide, and sulfate) were removed, while organic components were almost unchanged [34].

Ion-exchangeable cations in XLT (HF) were removed by mixing 0.5 g sample with 50 mL HCl aqueous solution (5 mol/L), and then the mixture was filtered and rinsed with 3 × 40 mL distilled water. The filtrate was made up to 200 mL, and the contents of cations in filtrate were measured by ICP-AES. Contents of cations in XLT (HF) are shown in Table 3. The content of cations was too low to be measured for XLT (HF HCl), HLGL (HCl HF), and HLGL (HCl).

CAQ in HLGL (HCl) were removed by HF aqueous solution, and then the mixture was filtered and rinsed with distilled water until no F⁻ was detected. The residual DMC was dried for 8 h under vacuum at 110 °C. The mass of CAQ in coal was calculated by the weight-loss after demineralization. The contents of CAQ in all the samples are listed in Table 4.

The contents of carboxyl groups and carboxylates were measured, and the results are shown in Table 5. The procedure of the measurement was similar to the one of Shafer [35]. The contents of carboxylates and total carboxyl groups were determined by mixing raw and demineralized coals with perchloric acid, respectively, and then titrating the residual acid in filtrate. The amount of carboxylates or total

Table 1
Proximate and ultimate analyses (wt%) of the coal samples.

Sample	Proximate analysis (d)			Ultimate analysis (daf)				S _t (d)
	A	V	FC	C	H	O*	N	
XLT	8.2 ± 0.2	49.2 ± 1.3	42.6 ± 1.5	66.8 ± 1.5	4.9 ± 0.1	>24.8	1.2 ± 0.1	0.5 ± 0.1
XLT (HF)	4.9 ± 0.1	52.9 ± 1.0	42.2 ± 1.1	61.9 ± 1.4	5.0 ± 0.1	>29.6	1.1 ± 0.2	0.6 ± 0.1
XLT (HF HCl)	0.5 ± 0.1	54.2 ± 0.9	45.3 ± 1.0	65.9 ± 1.1	5.2 ± 0.3	>25.5	1.2 ± 0.2	0.5 ± 0.1
HLGL	14.2 ± 0.4	40.5 ± 0.7	45.31 ± 1.1	68.2 ± 0.8	4.7 ± 0.2	>22.7	1.1 ± 0.3	0.8 ± 0.2
HLGL (HCl)	10.1 ± 0.3	42.8 ± 0.9	47.1 ± 1.3	67.9 ± 1.2	5.0 ± 0.1	>23.6	1.2 ± 0.1	0.7 ± 0.2
HLGL (HCl HF)	0.5 ± 0.1	45.7 ± 1.1	53.8 ± 1.2	67.5 ± 0.9	4.7 ± 0.1	>24.9	1.0 ± 0.2	0.6 ± 0.1

Note: daf, dry and ash free; d, dry basis; A, ash; V, volatile matters; FC, fixed carbon; S_t, total sulfur.

* By difference.

Download English Version:

<https://daneshyari.com/en/article/209064>

Download Persian Version:

<https://daneshyari.com/article/209064>

[Daneshyari.com](https://daneshyari.com)